



Article Nano-Structured Polyaniline as a Potential Adsorbent for Methylene Blue Dye Removal from Effluent

Monika Duhan¹ and Raminder Kaur^{2,*}

- ¹ Department of Applied Chemistry, Delhi Technological University, Delhi 110042, India; mduhandeswal@gmail.com
- ² Department of Polymer Science and Chemical Technology, Delhi Technological University, Delhi 110042, India
- Correspondence: rkwaliadtu@gmail.com

Abstract: The textile sector is one of the major culprits of water pollution, and demands immediate attention. The coloured textile effluent, loaded with toxic dyes, when mixed with waterbodies, may harm aquatic life, plants, animals, and humans. Although polyaniline in its different forms was utilised for the adsorption of different dyes, the pure nano-fibrous form of polyaniline, i.e., PANI nanofibers, have reportedly not been used for the removal of dyes from wastewater. The present study aimed to employ nano-structured polyaniline, in the form of polyaniline nanofibers (base; PNB—polyaniline nanofiber base) for the elimination of methylene blue (cationic dye; MB) dye from its solution. The polyaniline nanofiber base (PNB) was synthesised by an interfacial polymerisation technique using ammonium persulphate as the oxidant and toluene as the organic solvent, and was characterised by FTIR, SEM, BET, HRTEM and XRD techniques. The HRTEM and SEM results showed that the average size of the synthesised polyaniline nanofiber base (PNB) was about 60 nm. BET revealed the enhanced surface area of polyaniline nanofiber base (PNB), i.e., 48 m^2g^{-1} in comparison to that of conventionally synthesised polyaniline, which is only $14 \text{ m}^2\text{g}^{-1}$. The electric conductivity of the polyaniline nanofiber base (PNB) was reportedly lesser (2.3 \times 10⁻² S/cm) than the salt form of the polyaniline, measured by four probe technique. The batch-wise adsorption of MB was conducted onto the polyaniline nanofiber base (PNB), and the influence of the preliminary dye concentration, duration of contact and polyaniline nanofiber base (PNB) dose, etc., were studied. The equilibrium values of these parameters are reported as 6 mg/L, 60 min and 2 g/L, respectively. The results revealed the 91% sorption of dye onto the polyaniline nanofiber base (PNB). The experimental data were best-fitted to Pseudo-second order ($R^2 = 0.99$) and followed Freundlich isotherm model ($R^2 = 0.97$). On desorption, about 86% of the absorbed dye was recovered and the regenerated adsorbent could be used efficiently for three more cycles.

Keywords: adsorption; isotherm; kinetics; methylene blue; polyaniline nanofibers

1. Introduction

Hazardous waste released by various industries is the main focus of concern, because, if not treated appropriately, it can cause a threat to the environment and mankind. The textile sector releases a large volume of untreated wastewater into water bodies, which contains toxic dyes and chemicals that affect human beings, plants, and animals. The synthetic dyes not only impart colour to the water and introduce poisonous chemicals, they are also non-biodegradable, being resistant to the attack of microbes and light. Studies have shown that more than 10,000 tonnes/year of dyes are consumed around the world, and out of this amount, roughly 100 tonnes/year of dyes are lost in the textile effluent [1]. However, several water-treatment methods, namely, membrane separation, adsorption, coagulation/flocculation, oxidation, ozonation, microbes, etc., are employed for the management of wastewater from textile industries. The literature reveals that adsorption is the most effective technique for the eradication of dyes from the effluent due to it being affordable,



Citation: Duhan, M.; Kaur, R. Nano-Structured Polyaniline as a Potential Adsorbent for Methylene Blue Dye Removal from Effluent. *J. Compos. Sci.* **2021**, *5*, 7. https:// doi.org/10.3390/jcs5010007

Received: 18 December 2020 Accepted: 28 December 2020 Published: 31 December 2020

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/). more convenient and simplicity in operation [2,3]. Many studies have been conducted, and researchers have developed a variety of adsorbents from different precursors, such as agriculture by-products, natural materials, and solid industrial waste, and have tested their possibility for lowering the dye concentration in wastewater [4]. However, many of these adsorbents have not been explored extensively at the industrial level due to some operational instability. Since 2005, polyaniline (PANI), which was originally recognised and used as a conducting polymer [5,6], has attracted the attention of researchers as an adsorbent, with its improved properties, such as a larger surface area, modified mechanical properties, low cost, high adsorption capacity and simple preparation. Literature reveals that, although polyaniline in its different forms (i.e., acidic (ES) and basic forms; PANI composites; coatings of PANI on different solid substrates; salt forms of PANI; and doped PANI) have reportedly been used as adsorbents for dyes and other organic compounds, the nano-structured polyaniline in the form of nanofibers has rarely been explored for the adsorption of dyes [4].

Methylene blue (MB) is among the most commonly used dyes in the textile industry. Additionally, it is a widely used dye in the chemical and medical sectors. Though not lethal, its prolonged usage may lead to vomiting, nausea, dizziness or hypertension [3,7]. Different adsorbents have been suggested in the literature for the removal of MB dye from its aqueous solution, along with their percentage removal, such as: tobacco stem ash (81%) [8], fly ash (45%) [9], pine leaves (80%) [1], kaolite (90%) [10], etc. Taking into account the above facts, the current research focused on the absorption of methylene blue dye onto nano-structured polyaniline (polyaniline nanofibers), due to its remarkable physicochemical properties. The influence of dye's initial concentration, polyaniline nanofiber base (PNB) dose and contact period have been explored, along with the study of the reaction kinetics and isotherm fitting.

2. Materials and Methods

2.1. Materials

Aniline (supplied by CDH, New Delhi, India), Ammonium persulfate (APS)[(NH₄)₂S₂ O₈] (supplied by CDH, New Delhi, India), methylene blue: (M.Wt. 319.85 g/mol, λ_{max} : 664 nm) (supplied by CDH, New Delhi, India), hydrochloric acid (supplied by Rankem, Bengaluru, India), and toluene (supplied by CDH, New Delhi, India), all of AR grade were used. Dye solutions were prepared in distilled water, supplied by the Applied Chemistry Lab, DTU, Delhi, India.

2.2. Synthesis of Adsorbent

Polyaniline nanofibers were synthesised by interfacial polymerisation method [11,12]. In brief, 0.32 mol of monomer (aniline) was dissolved in toluene in a beaker to form the organic phase. The aqueous phase was formed by dissolving 0.08 mol of APS in 1M HCl solution in another beaker. The APS solution was added dropwise to the organic phase, within a specific period of time, and then kept undisturbed for a period of 20 h. The content was filtered and washed repeatedly using distilled water. The base form of the polyaniline was achieved by reacting the above mixture with ammonia (1M). The obtained blue coloured compound was dried at 60 $^{\circ}$ C for 24 h. A polyaniline nanofiber base (PNB) in the powder form was obtained.

2.3. Characterisation of the Adsorbent

The synthesised adsorbent was examined for its morphology by using scanning electron microscopy (SEM) (make: S-3700 N; Hitachi, Japan). Transmission electron microscopy (TEM) analysis confirmed the size of the adsorbent, using ethanol-dispersed PANI samples on a standard copper grid and taking images on an F 30 S twin 300 HRTEM at 300 kV. FTIR spectra of the synthesised PNB within a wavenumber range of 400–4000 cm⁻¹ and at 25 °C was recorded by Nicolet 380 FT-IR spectrophotometer. BRUKER D8 ADVANCE diffractometer, at 40 mA and 40 kVA was employed to examine the X-ray diffraction (XRD)

pattern of PNB (adsorbent), by using CuK α (K α =1.54056 Å) radiation and the scanning pace of 0.02⁰ in 2 θ and a reside span of 0.5 s per step. The electrical conductivity of the synthesised nanofibers was measured by four point probe apparatus with digital microvoltmeter, current source, and an oven with PID control. The surface area of the adsorbent was investigated with the BET Surface Area Analyser (Micrometrics ASAP 2010, Verneuil Halatte, France). The adsorptive studies of the dye were carried out using a UV–Vis spectrophotometer (Agilent Technologies, Santa Clara, CA, USA) with an operating wavelength within the 200–800 nm range, after calibrating it with standard dye (MB) solutions.

2.4. Adsorptive Studies of Dye onto PNB

Firstly, the standard solution of the methylene blue dye (10 mg/L) was prepared. Subsequently, this stock solution was diluted to obtain dye solutions of varying concentrations (2–9 mg/L) by adding calculated volumes of distilled water. The adsorptive studies were conducted in batch mode, each using a fixed volume of dye (20 mL) and adsorbent (0.01–0.1 g), as calculated, by agitation at the desired rpm in an incubator shaker, for a fixed time period (up to 120 min), followed by the centrifugation of the reaction mixture for 15 min, at 8733 rcf. The dye remained un-adsorbed, and was then assessed by UV–Visible spectroscopy at a wavelength of 664 nm. In parallel, the solutions of individual concentrations were estimated at λ_{max} 664 nm. Then, the concentration data vs. absorbance data were plotted. Equations (1) and (2) were employed to investigate the adsorption capacity and the percentage of dye adsorbed onto the polyaniline nanofiber base (PNB), respectively.

$$Q = \frac{(C_o - C_e)V}{m} \tag{1}$$

$$\% A = \frac{C_o - C_e}{m} \times 100\%$$
 (2)

where Q (mg/g) is the adsorption capacity, $C_o \text{ (mg/L)}$ is the initial dye concentration, $C_e \text{ (mg/L)}$ is the equilibrium dye concentration, V (L) is the volume of dye used, and m (g) is the mass of the PNB adsorbent used per batch.

3. Results

3.1. Characterisation

The nature of the polyaniline nanofiber base (crystalline or amorphous) was detected by XRD (Figure 1). The diffraction pattern shows two diffraction peaks at 20 values of 18° and 23.5°, respectively. The peaks at about 18° and 23.5° are due to periodicity parallel and perpendicular to the main chain of adsorbent, respectively. The crystal size of the polyaniline nanofiber base (PNB) adsorbent was calculated by the Debye Scherer equation (Equation (3) below), which was determined as 3.5 nm:

$$D = \frac{K\lambda}{(\beta COS\theta)} \tag{3}$$

where β is the full width half maximum (FWHM), and *K* is Bragg's constant (0.9).

According to the observed peaks (due to quinonoid and benzenoid groups) in the XRD pattern, PANI nanofibers are dominantly amorphous in nature. Similar studies were also carried out by other researchers. [13,14].

FTIR spectra of the polyaniline nanofiber base (PNB) adsorbent are given in Figure 2. The peak at 3250 cm^{-1} is attributed to N–H stretching. The absorption band centred at 2981 cm⁻¹ signifies the asymmetric stretching corresponding to the C–H link of the aromatic bond. The bands at 1567 cm^{-1} and 1489 cm^{-1} , show respectively, the C=C stretching of the quinoid and benzenoid ring, which confirms the emeraldine agreement of polyaniline. The absorption peak at 1444 cm^{-1} is linked to C=N aromatic stretching. The band at 1288 cm^{-1} reveals the C–N stretching of the secondary aromatic amine, whereas the vibration band at 1144 cm^{-1} is attributed to the in-plane bending of C–H. The pulsation

peaks at 820 cm⁻¹ and 740 cm⁻¹ denotes the out-of-plane C–H deformation in the 1,4 di-substituted benzene ring. The above vibration bands of polyaniline are also confirmed by the existing literature studies [15].



Figure 1. XRD pattern of polyaniline nanofibers.



Figure 2. FTIR Spectra of the PNB adsorbent.

The surface morphology of the synthesised polyaniline nanofiber base (PNB) was confirmed by the results of SEM analysis (Figure 3a,b). The average diameter of the PANI nanofibers was identified as 60 ± 5 nm. Previous studies also revealed the synthesis of polyaniline nanofibers of 30–60 nm in size by using an interfacial polymerisation method [16,17]. Likewise, the HRTEM images (Figure 3c,d) also supported the nanostructure of the polyaniline nanofiber base (PNB), and reported the presence of roughness on its surface. Furthermore, the outcomes of the BET analysis evidenced the improved surface area in the case of the polyaniline nanofiber base (PNB) in comparison to the conventionally synthesised polyaniline, which established it as more favourable to be used as an adsorbent. The pore diameter surface area and pore volume of both the polyaniline nanofiber base (PNB) and the conventional polyaniline are reported in Table 1. The results of the four probe technique show that the synthesised polyaniline nanofiber base (PNB) had less electrical conductivity (2.3×10^{-2} S/cm) as compared to its salt form. The attained results are in good agreement with those found in the existing literature [18] for the emeraldine base form of the polyaniline.



Figure 3. (a) and (b) SEM analysis and (c) 200 nm and (d) 50 nm HRTEM analysis of the PNB adsorbent.

Table 1. Data of the BET analyses for the PNB adsorbent and conventional polya	niline.
---	---------

Adsorbent	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Diameter (nm)
Polyaniline Nanofibers	48	1.0256×10^{-2}	15.7
Conventional Polyaniline	14	$2.638 imes10^{-3}$	34.4

3.2. Adsorption Studies

The capability of the polyaniline nanofiber base (PNB) to eliminate MB dye from its solution was recognised by conducting absorptive studies in batch mode. For this, 0.04 g of the adsorbent polyaniline nanofiber base (PNB) was added to 20 mL of dye solution. The adsorption parameters were taken as: temperature = $35 \degree C$, RPM = 250, pH = 7, and initial dye concentration = 6 mg/L. The adsorption process is influenced by the contact time, therefore the adsorption of MB dye onto the polyaniline nanofiber base (PNB) was investigated by varying the contact time and is reported in Figure 4a. As seen from the plot, with increasing the contact time, the adsorption of the dye increased, and about 79% of the dye was reportedly adsorbed within the first 20 min of the contact. After 60 min, the equilibrium was achieved, with about 90% of the dye removed. Thus, the equilibrium contact time for the adsorption system of MB onto PNB was reported as 60 min. Furthermore, on studying, the influence of varying the initial dye concentrations (2-10 mg/L) on the adsorption of MB on the polyaniline nanofiber base (PNB), keeping the other parameters fixed (adsorbent dose = 0.04 g, contact time = 60 min, pH = 7, and temperature = $35 \degree$ C), the curve obtained is as shown in Figure 4b, which signifies the percentage decrease in adsorption with the rise in initial concentration of the dye. The reason for this decrease is the availability of more dye molecules, due to increased dye concentration, which, on adsorption, occupied the majority of the available active sites, and thus, left the excess dye molecules in the solution itself. On the contrary, the equilibrium dye adsorption increased with the increased dye concentration because of the enhanced driving force supplied by the additional dye molecules to overcome the mass transfer resistance between the solid adsorbent phase and

aqueous dye phase. In addition, the increased initial dye concentration also favoured the enhanced adsorbent–adsorbate (dye) interactions. From the experimental studies, it has been observed that no noteworthy change in the MB adsorption was achieved beyond the initial dye concentration of 6 mg/L, and thus, 6 mg/L was considered as the equilibrium concentration value for MB adsorption onto the PNB adsorbent. The literature studies also highlighted the analogous patterns for the different dye adsorptions, including methyl orange, methyl violet, and reactive blue 221 [19,20].



Figure 4. Plots of (a) contact time; (b) initial dye concentration, and (c) PNB dose vs. adsorption for a PNB-MB adsorption system.

Another important parameter in the adsorption experiments is the dose (amount) of adsorbent used. The outcome of the polyaniline nanofiber base (PNB) dosage on the adsorption of MB dye (Figure 4c) was studied, and an increase in the adsorption percentage was observed from 64% to 93%, with the variation in polyaniline nanofiber base (PNB) dose from 0.01–0.1 g, keeping the values of other parameters constant. Initially, the adsorption percentage of dye increased rapidly with the adsorbent dosage, and after a certain point, no significant adsorption was progressed, i.e., beyond a constant value of 0.04 g (for 20 mL dye solution). Therefore, the optimised value of the adsorbent dose was calculated as 2 g/L for this study. Greater dye removal was justified by the accessibility of a greater surface area and number of active sites on the adsorbent, at a higher adsorbent dose. The above results are in agreement with the studies on methyl blue dye removal by activated carbon [21].

3.3. Kinetic Studies of MB Adsorption onto a Polyaniline Nanofiber Base (PNB)

The adsorption of MB dye onto a polyaniline nanofiber base (PNB) was analysed by using the already established models; pseudo-first order model, pseudo-second order model and intra-particle diffusion model.

Equation (4) is for a pseudo-first order model:

$$log(Q_e - Q_t) = \log Q_e - \frac{K_1 t}{2.303}$$
(4)

where Q_e (mg/g) is the dye adsorbed onto PNB, at equilibrium, Q_t (mg/g) is the dye adsorbed onto PNB at time equal to *t* (min), and K_1 (L/min) is the first order rate constant.

The suitability of the pseudo-first order model for the adsorption of MB onto the polyaniline nanofiber base (PNB) was examined by plotting log ($Q_e - Q_t$) vs. t. The best fit straight line can be seen in Figure 5a. The rate constant, K_1 and equilibrium dye adsorption, Q_e can be obtained from the slope and intercept of the plot, respectively. Table 2 reports the values of the various adsorption parameters for the pseudo-first order model, for the MB–PNB adsorption system. The R² value obtained from the above plot is equal to 0.91. However, the calculated and the experimental Q_e values do not match well, thus,



the pseudo-first order model, does not seem to provide satisfactory justification for the adsorption of MB dye onto the PNB adsorbent.

Figure 5. Kinetics of the PNB–MB adsorption system by: (**a**) pseudo-first order model; (**b**) pseudo-second order model; and (**c**) intra-particle diffusion model.

Kinetic Models	Parameters	R ² Value
Pseudo-first order	$K_1(\min^{-1})$ —0.087 $Q_e, \exp(\operatorname{mg} g^{-1})$ —8.63 $Q_e, \operatorname{cal}(\operatorname{mg} g^{-1})$ —9	0.91
Pseudo-second order	$K_2 (g mg^{-1} min^{-1})$ —0.0046 Q_e , cal(mg g ⁻¹)—9.52	0.99
Intra-particle diffusion	$K_{\rm i} \ ({\rm mg \ min}^{0.5} {\rm \ g}^{-1}) - 0.22 \ C - 7.02$	0.82

Subsequently, the adsorption data were fitted into the pseudo-second order model (Equation (5)), as:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \tag{5}$$

where Q_e (mg/g) is the dye adsorbed onto PNB, at equilibrium, Q_t (mg/g) is the dye adsorbed onto PNB at time equal to t (min), and K_2 (g/mg min) is the second order rate constant.

The adsorption data were plotted as t/Q_t vs. t. The best fit straight line is shown in Figure 5b. The different adsorption parameters for the pseudo second order model have been recorded in Table 2. From the result, it is clear that the experimental and calculated Q_e values are in good agreement. Moreover, the R² value obtained from this plot was 0.99. Thus, the pseudo second order model was the best fitted model for the MB adsorption onto the polyaniline nanofiber base (PNB) adsorbent, which, in turn signifies that the adsorption system is favoured by chemisorption.

The data of the MB–PNB adsorption system were also tested for the suitability of intra-particle diffusion model, represented by Equation (6):

$$Q_t = K_i t^{0.5} + C \tag{6}$$

where Q_t (mg/g) is the dye adsorbed onto PNB at time equal to t (min), K_i (mg/g min^{0.5}) is the rate constant for intra-particle diffusion, and C is the boundary layer thickness.

The adsorption data of MB on PNB, plotted as Q_t vs. $t^{0.5}$, are shown in Figure 5c. K_i and C can be obtained from the slope and the intercept of the best fit straight line, respectively. All adsorption parameters are reported in Table 2.

From Figure 5c, because the best fitted straight line does not pass through the origin and its R^2 value (0.82) is also quite small, the intra-particle model is not the sole model followed by MB–PNB adsorption system, although it plays a substantial role in combination with other mechanism(s).

Adsorption in the MB–PNB system occurred mainly by the involvement of electrostatic interactions between the positive charge of the dye and lone pairs of electrons residing on the nitrogen atom of the polyaniline backbone, H-bonding, and π – π interactions. A schematic representation of the interactions involved for the MB–PNB adsorption system is shown in Figure 6. The positively charged moiety of the methyl blue dye interacts with lone pairs of amine nitrogen electrons of the backbone of the polyaniline base (electrostatic interactions) and π – π interactions exist between the aromatic rings of polyaniline and methylene blue dye. Additionally, the H-bonding between the two participants enhances the removal of MB by the polyaniline nanofiber base (PNB).



Figure 6. Schematic representation of interactions in the PNB-MB adsorption system.

3.4. Isotherm Studies

To realise the dispersal of the adsorbate onto the adsorbent surface, isotherm studies were conducted. The adsorption of MB onto the polyaniline nanofiber base (PNB) has been explored by both Langmuir and Freundlich isotherms. As per the Langmuir isotherm model, the adsorbate forms a monolayer over the adsorbent surface. The equation for the Langmuir isotherm is as follows:

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{1}{Q_m}C_e \tag{7}$$

where C_e (mg/L) is the dye Concentration, Q_m (mg/g) is the maximal adsorption capacity (for complete monolayer spread), Q_e (mg/g) is the equilibrium adsorption capacity, and b (L/mg) is the Langmuir constant.

The plot of $\frac{C_e}{Q_e}$ vs C_e is shown in Figure 7a. The slope and intercept of the best-fitted line gives the Q_m and b values, respectively. All the adsorption parameters are reported in Table 3. From the value of R² (0.66), it is evident that the Langmuir isotherm model is not in agreement with the adsorption of MB onto PNB. The dimensionless factor (R_L), equal to 0.26, as evaluated from Equation (8) below, for the viability of the adsorption, also indicates

that the elimination of MB by using the polyaniline nanofiber base (PNB) adsorbent cannot be justified by Langmuir's isotherm model:

$$R_L = \frac{1}{1 + bC_o} \tag{8}$$



1

Figure 7. The isotherm studies of MB on PNB by using: (a) Langmuir model, and (b) the Freundlich model.

Table 3. Adsorption parameters for MB onto the PNB adsorbent for both the Langmuir and Freundlich models.

Isotherms	Isotherm Constant	R ² Value
Langmuir	Q_m —24.3 b—0.64 R_L —0.26	0.66
Freundlich	K_{f} —9.72 n_{h} —1.29	0.97

The Freundlich model is concerned mainly with the adsorption on heterogeneous surfaces, in contrary to those on homogeneous surface. Equation (9) is used to represent the Freundlich isotherm model:

$$\log Q_e = \log K_f + n_h \log C_e \tag{9}$$

where $Q_e (mg/g)$ is the equilibrium adsorption capacity, $C_e (mg/L)$ is the dye concentration, K_f is the Freundlich constant (which expresses the maximum adsorption capacity), and n_h is the Freundlich constant.

Figure 7b displays the log Q_e vs. log C_e relationships for the adsorption of MB onto PNB. As demonstrated from the plot and R² value (0.98), the Freundlich isotherm model is the best-suited isotherm model. All the other adsorption parameters are depicted in Table 3. The favourability of the Freundlich isotherm clearly signifies that the adsorption of dye has been carried out on the heterogeneous surface of polyaniline nanofiber base (PNB), with the formation of multilayers. Similar results are reported in the literature, for the adsorption of MB on the doped form of polyaniline nanofibers [22].

4. Desorption Studies

Desorption studies were conducted to utilise the adsorbed dye and to regenerate the exhausted adsorbent. The dye (MB)-loaded polyaniline nanofiber base (PNB) was treated with various solvents such as 0.1 M NaOH, distilled water, 95% ethanol and 0.1 M HCl. Amongst all the solvents explored for the desorption, ethanol (95%) worked the best. It was found that about 86% of the adsorbed dye was recovered. The results obtained in this study are better as compared to a reported study on an MB–black tea powder adsorption

system [23], where the recovery of MB was only 75%. Moreover, the recovered adsorbent was found to be effective, with readily active sites, and can be re-utilised for three more cycles of adsorption without much compromise in its adsorption capacity.

5. Conclusions

The nano-structured polyaniline, as a base form of polyaniline nanofibers (PNB), was explored as an adsorbent for the methylene blue (MB) dye elimination. PNB adsorbent was synthesised by interfacial polymerisation technique, and characterised by SEM, FTIR, HRTEM, BET, XRD, and four probe techniques. The adsorption studies were conducted in a batch-wise manner, and the adsorption analysis was carried out using UV–Visible spectroscopy. The reaction kinetics were investigated using pseudo-first order, pseudosecond order, and intra-particle diffusion models. The adsorption data were found be best fitted in the pseudo-second order model, thus indicating that the adsorption of MB on the polyaniline nanofiber base (PNB) was dominated by chemisorption. Both Langmuir and Freundlich isotherm models were tested to analyse the equilibrium data. The Freundlich isotherm was reported to be the best-fitting model for this adsorption system, thus confirming the monolayer formation of the MB dye onto the heterogeneous surface of the PNB adsorbent. It was detected that approximately 91% of the methylene blue dye was removed by the polyaniline nanofibers. The influence of adsorption parameters, i.e., initial dye concentration, time of contact and adsorbent dosage were also examined, and their equilibrium values are reported as 6 mg/L, 60 min and 2 g/L, respectively. About 86% of the adsorbed dye was recovered in the desorption studies and the adsorbent was found to be working satisfactorily up to the fourth cycle of adsorption. Thus, the nano-structured base form of polyaniline nanofibers is a promising adsorbent for the removal of basic/cationic dyes from wastewater effluent.

Author Contributions: Conceptualization, R.K.; Data curation, M.D.; Formal analysis, M.D.; Investigation, M.D.; Methodology, R.K.; Supervision, R.K.; Writing—original draft, M.D.; Writing—review & editing, R.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: This manuscript does not contain shared data.

Acknowledgments: We are thankful to Delhi Technological University for providing us with necessary facilities to conduct these studies.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Yagub, M.T.; Sen, T.K.; Ang, H. Equilibrium, kinetics, and thermodynamics of methylene blue adsorption by pine tree leaves. Water Air Soil Pollut. 2012, 223, 5267. [CrossRef]
- Wong, S.; Ghafar, N.A.; Ngadi, N.; Razmi, F.A.; Inuwa, I.M.; Mat, R.; Amin, N.A.S. Effective removal of anionic textile dyes using adsorbent synthesized from coffee waste. *Sci. Rep.* 2020, *10*, 2928. [CrossRef]
- Mohammed, M.A.; Shitu, A.; Ibrahim, A. Removal of Methylene Blue Using Low-Cost Adsorbent: A Review. *Res. J. Chem. Sci.* 2014, 4, 91.
- 4. Kaur, R.; Duhan, M. Polyaniline as an inceptive dye adsorbent from effluent. In *Advanced Materials for Wastewater Treatment*; Tiwari, A., Ed.; Wiley: Hoboken, NJ, USA, 2017; pp. 51–100.
- Ali, V.; Kaur, R.; Kamal, N.; Singh, S.; Jain, S.C.; Kang, H.P.S.; Zuifequer, M.; Husain, M. Use of Cu⁺¹ dopant and its doping effects on polyaniline conducting system in water and tetrahydrofuran. *J. Phys. Chem. Sol.* 2006, 67, 659. [CrossRef]
- Ali, V.; Kaur, R.; Lakshmi, G.B.V.S.; Kumar, A.; Kumari, K.; Kumar, S. Electrical conductivity and dielectric parameters of polyaniline doped with CuClO₄.4BN in aqueous DMSO solvent. *Adv. Polym. Technol.* 2012, *31*, 374. [CrossRef]
- 7. El-Sharkaway, E.A.; Kamel, R.M.; El-Sherbiny, I.M.; Gharib, S.S. Removal of methylene blue from aqueous solutions using polyaniline/graphene oxide or polyaniline/reduced graphene oxide composites. *Environ. Technol.* **2019**, *21*, 1. [CrossRef]
- 8. Ghosh, R.K.; Reddy, D.D. Tobacco Stem Ash as an adsorbent for removal of methylene blue from aqueous solution: Equilibrium, kinetics, and mechanism of adsorption. *Water Air Soil Pollut.* **2013**, 224, 1. [CrossRef]
- 9. Kumar, K.V.; Ramamurthi, V.; Sivanesan, S. Modeling the mechanism involved during the sorption of methylene blue onto fly ash. *J. Colloid Interface Sci.* 2005, 284, 14. [CrossRef]

- 10. Tehrani-Bagha, A.R.; Nikkar, H.; Mahmoodi, N.M.; Menger, F.M. The sorption of cationic dyes onto kaolin: Kinetic, isotherm and thermodynamic studies. *Desalination* **2011**, *266*, 274. [CrossRef]
- 11. Huang, J.; Virji, S.; Weiller, B.H.; Kaner, R.B. Polyaniline nanofibers: Facile synthesis and chemical sensors. *J. Am. Chem. Soc.* 2003, 125, 314. [CrossRef]
- Duhan, M.; Kaur, R.; Nagpal, A. Adsorptive Removal of Methylene Blue by Polyaniline Nanofibers. In Proceedings of the 1st International Conference on New Frontiers in Engineering, Science & Technology, New Delhi, India, 8–12 January 2018; ISBN 978-93-86238-41-2.
- 13. Morsi1, R.E.; Elsabee, M.Z. Polyaniline Nanotubes: Mercury and Competative Heavy Metals Uptake. *Am. J. Polym. Sci.* 2015, *5*, 10–17.
- 14. Kavitha, B.; Siva Kumar, K.; Narsimlu, N. Synthesis and characterization of polyaniline nano-fibers. *Indian J. Pure Appl. Phys.* **2013**, *51*, 207–209.
- 15. Vivekanandan, J.; Ponnusamy, V.; Mahudeswaran, A.; Vijayanand, V.P.S. Synthesis, characterization and conductivity study of polyaniline prepared by chemical oxidative and electrochemical methods. *Arch. Appl. Sci. Res.* **2011**, *3*, 147.
- 16. Duhan, M.; Kaur, R. Adsorptive removal of methyl orange with polyaniline nanofibers: An unconventional adsorbent for water treatment. *Environ. Technol.* **2020**, *41*, 2977. [CrossRef] [PubMed]
- 17. Zhang, X.; Chan-Yu-King, R.A.; Manohar, S.K. Nanofibers of polyaniline synthesized by interfacial polymerization. *Synth. Met.* **2004**, *145*, 23. [CrossRef]
- 18. Chauhan, N.P.S.; Ameta, R.; Ameta, R.; Ameta, S.C. Thermal and conducting. behaviour of emeraldine base (EB) form of polyaniline (PANI). *Indian J. Chem. Technol.* **2011**, *18*, 118.
- 19. Chen, S.H.; Zhang, J.; Zhang, C.L.; Yue, Q.Y.; Li, Y.; Li, C. Equilibrium and kinetic studies of methyl orange and methyl violet adsorption on activated carbon derived from *Phragmites australis*. *Desalination* **2010**, 252, 149. [CrossRef]
- Karaoglu, M.H.; Dogan, M.; Alkan, M. Kinetic analysis of reactive blue 221 adsorption on kaolinite. *Desalination* 2010, 256, 154. [CrossRef]
- Kannan, N.; Sundaram, M.M. Kinetics and Mechanism of Removal of Methylene Blue by Adsorption on Various Carbons— A Comparative Study. *Dyes Pigments* 2001, 51, 25. [CrossRef]
- 22. Duhan, M.; Kaur, R. Phytic acid doped polyaniline nanofibers: An advanced adsorbent for methylene blue dye. *Environ. Nanotechnol. Monitor. Manag.* 2019, 12, 1. [CrossRef]
- 23. Lin, D.; Wu, F.; Hu, Y.; Zhang, T.; Liu, C.; Hu, Q.; Hu, Y.; Xue, Z.; Han, H.; Ko, T.H. Adsorption of Dye by Waste Black Tea Powder: Parameters, Kinetic, Equilibrium, and Thermodynamic Studies. *J. Chem.* **2020**, *2020*, 5431046. [CrossRef]